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Supercritical Fluid Extraction of Dry-Milled Corn Germ with Carbon Dioxide

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ABSTRACT

Dry-milled corn germ was extracted with supercritical carbon dioxide (SC-CO_2) at 5,000–8,000 psi and 50°C. CO_2-extracted oil was lower in free fatty acids and refining loss, and was lighter in color when compared with a commercial expeller-milled crude oil. Total unsaponifiable and tocopherol contents were similar for both oil types. The defatted, highly friable flour has a shelf-stable moisture content of 2–3% and good flavor quality. The flour contains 20% protein with good amino acid balance, meeting FAO specifications for food protein supplements. High pressure SC-CO_2 extraction also denatures the proteins, including oxidative enzymes. Peroxidase activity is reduced tenfold in SC-CO_2-extracted flour when compared with hexane-extracted flours. Storage tests for 5 wk at 38°C and for 2 months at 25°C show that flavor quality of untoasted SC-CO_2-defatted germ flour is maintained even under these extreme conditions.

INTRODUCTION

SELLING FARM COMMODITIES in a higher valued, more finished form than is now customary could expand world markets for U.S. farm products (Delano, 1982). The primary problem in developing more finished vegetable protein products is the need to control deterioration during long storage periods needed for shipment and distribution. At present, conventional oil extraction solvent leaves certain lipids in the flour that either auto- or enzymically oxidize into off-flavor compounds during storage and reduce the flavor and nutritional quality of the product. New research approaches to extract oil and methods to improve shelf life of defatted flours are needed.

The recent application of critical fluids as extracting agents in industrial processes led Stahl et al. (1980) to investigate the potential of supercritical gases for the extraction of oils from soy beans, sunflower seeds, and rapeseeds. The efficiency of extraction is dependent upon the time CO_2 is in contact with the ground seeds, upon size and physical structure of the seed particles, and upon pressure and temperature of extraction. In other studies, Stahl and Willing (1978) have shown that phenolics and other bitter-tasting compounds could also be extracted with SC-CO_2.

Recently, studies have been completed at our Center on SC-CO_2 extraction of oil from soybean flakes (Friedrich et al., 1982) and on the comparison of this oil with that obtained by hexane extraction (Friedrich and List, 1982). Oil yields by SC-CO_2 extraction were comparable to those of hexane-extracted oil. The SC-CO_2-extracted oil had significantly lower refining loss and phosphorous content, was light-colored and essentially degummed.

Numerous studies on the upgrading of defatted dry-milled corn germ flour into a food-grade product have been conducted since Wall et al. (1971) demonstrated that corn germ was an excellent source of balanced protein. The nutritional value of this corn germ flour as a protein-mineral food supplement has been reviewed (Gardner et al., 1971).

This paper reports the use of supercritical carbon dioxide in place of hexane for corn oil extraction and production of a food-grade quality defatted germ flour. The fate of minor bitter-tasting constituents and peroxidase enzymes and the flavor and storage characteristics of the residue flour are also discussed.

MATERIALS & METHODS

Materials

Commercial-grade carbon dioxide was obtained in 60-lb cylinders from Matheson (Joliet, IL). Full-fat, dry-milled germ containing 23.4% oil, 14.4% protein (N x 5.4), 6.8% ash, and 3.5% moisture was obtained commercially. Germ was stored at 37°F before use (maximum storage time less than one month). Expeller oil was also obtained commercially for preliminary comparison with SC-CO_2 extracted corn oil.

Extraction

A flow diagram of the extraction apparatus is shown in Fig. 1. A list of equipment manufacturers and description of the process were detailed earlier (Friedrich et al., 1982). The compressed CO_2 gas is passed through the flaked germ within the temperature-controlled vessel (50°C). Oil is extracted from the germ at 5,000 psig and 8,000 psig. At the bottom of the vessel the oil-laden SC-CO_2 is depressurized, and the dissolved oil separates and is collected in the receiver (50°C). Some moisture in the sample also is removed and vented with the decompressed CO_2 gas. Oil is removed from the receiver and weighed at timed intervals. The amount of CO_2 consumed in the extraction is determined at the same time by measuring the exhausted CO_2 with a dry test meter. Measurement of CO_2 and oil recovered at various intervals permitted calculation of oil recovery rates and oil solubility. Analysis and data reported are the average of two separate extractions. Extractions were performed on full-fat germ samples ranging from 450–1,000g. "As is" and tempered (8% moisture) samples were flaked through a smooth roller mill. Tempering was investigated because germ is more uniformly flaked when hydrated.

Analytical

Standard AOAC and AACC methods were used for the analyses of the SC-CO_2 extracted flours. The small amount of residual triglyceride oil remaining in the flours was determined by gas chromatography (Black et al., 1967). Nitrogen solubility index (NSI) was determined to establish what effect supercritical fluid extraction had on denaturation of germ proteins. Defatted germ flours were hydrolyzed in 6N HCl under reflux conditions for 24 hr. Amino acids contained in the hydrolyzed samples were chromatographically separated and analyzed on a Glenco 1000 amino acid analyzer. Amino acid compositions of the extracted germ flours were compared with FAO/WHO scoring patterns (1973).

Crude oils were analyzed for free fatty acids, phosphorus, refining loss, color, and unsaponifiable matter by official AOCS methods (AOCS, 1975). Total tocopherol content of extracted oils was determined by saponification of triglyceride contaminants (AOAC, 1980), followed by colorimetric analysis by the Emorline-Engel Method (Rawlings et al., 1948). Oxidative stability of the extracted oil was determined by measuring weight increases of the oil during storage at 60°C in a forced air oven similar to methods described by Olcott and Eiset (1958).

Sensory evaluation

Samples were rated for flavor intensity on a 10-point scale (10 as bland and 1 as strong) by a trained 15-member panel experienced in evaluating cereal and soy products. Descriptions of flavor listed on the score sheet include: cereal/grain, grassy/beany, musty/stale, bitter, and astringent. Flours were tested as 2% dispersions in charcoal-filtered tap water. Each tester received a 10-ml portion. Untoasted SC-CO_2 germ flours were compared

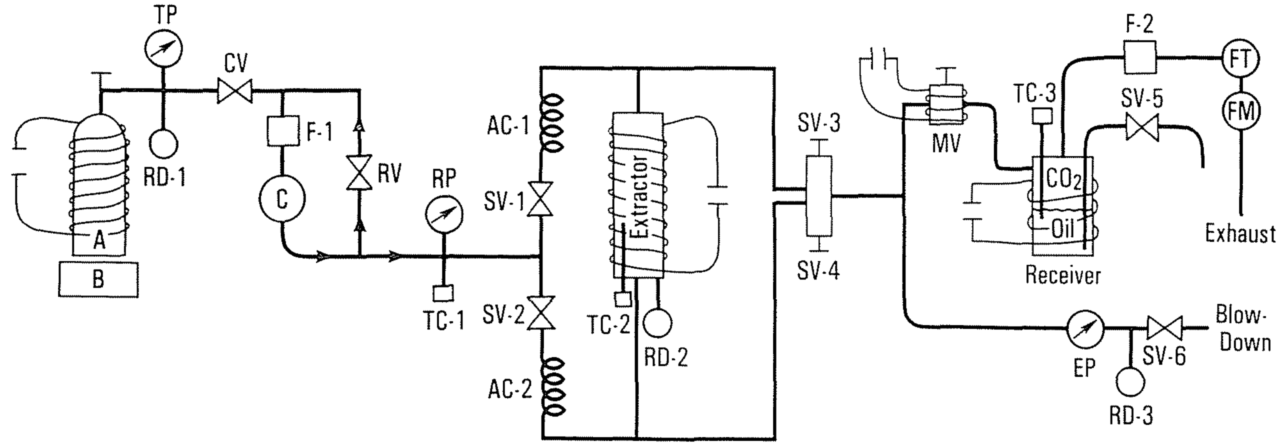

Fig 1—Supercritical carbon dioxide extraction apparatus: (A) CO_2 cylinder, (B) balance, (R) relay, (TP) tank pressure, (RD) rupture disk, (CV) check valve, (F) gas filters, (C) diaphragm compressor, (RV) back pressure regulating valve, (RP) regulated gas pressure, (TC) thermocouples, (SV) shut-off valve, (MV) micro-metering valve, (FM) flow meter, (FT) flow totalizer, and (EP) extractor pressure (Friedrich et al., 1982).

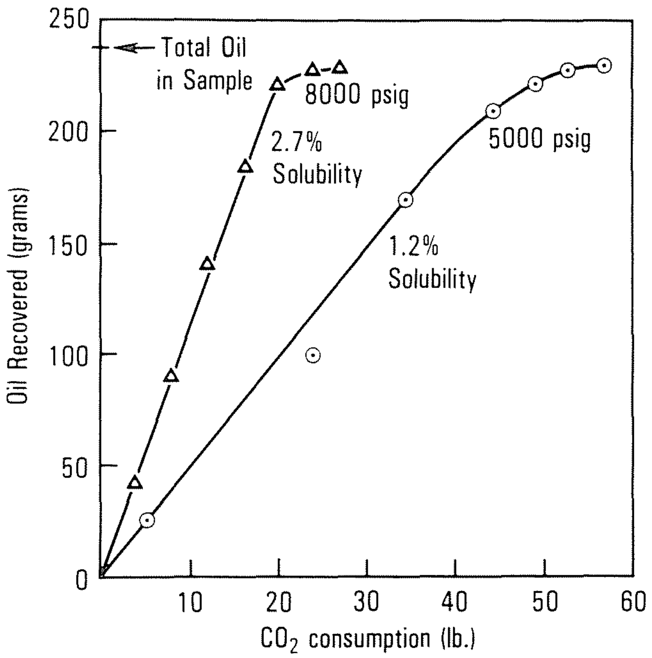

Fig 2—Supercritical extraction of 8% tempered and flaked dry-milled corn (1,000g) in a cylindrical vessel (2 liter); 2-7/16 in. i.d. × 29-1/4 in. long, at a CO_2 flow rate of 15–18 liter/min and a temperature of 50°C.

at 38°C for 5 wk and at 25°C for 8 wk. Storage test methods are similar to those used for corn-soy-milk blended foods (Bookwalter et al., 1971). Germ flours were stored at these temperatures in sealed glass bottles with minimal head space.

Panelists also described the flavors detected in the flours and rated their intensities on a 0 to 3 scale with 0 = none, 1 = weak, 2 = moderate, 3 = strong intensity. These flavor intensity values were weighted as shown in the following calculation:

$$\text{FIV} = \frac{1 \times \text{No. of weak responses} + 2 \times \text{No. of moderate response} + 3 \times \text{No. of strong responses}}{\text{No. of testers}}$$

Results

Flour Extraction

Fig. 2 shows the cumulative grams of oil removed from an 8% tempered germ sample, containing 23.4% oil, as a function of CO_2 (lb) passed through the extractor. The straight line portions of the 5000 and 8000 psig curves show the solubility (weight %) of the oil in CO_2.

The linearity of these plots shows constancy of oil solubility during the major portion of the extraction. When most of the oil has been removed, the slopes of the curves decrease and the plots approach the theoretical oil content asymptotically. The solubility at 5000 psig was 1.2% as compared to 2.7% at 8000 psig, which indicates that at constant temperature increasing the pressure improves extraction efficiency. Corn oil solubilities at these pressures and temperature (50°C) are similar to those obtained for soy oil extracted from soybean flakes (Friedrich et al., 1982). Apparently, tempering the germ to 8% moisture prior to flaking did not influence extraction solubility or recovery, because the germ flaked at 3.5% moisture ("as is") gave results similar to those shown in Fig. 2. Therefore, moisture at this level does not affect the extraction efficiency or the ultimate oil yield. While moisture content is an important factor in extraction of caffeine from coffee, it plays a lesser role in extraction of oil from corn dry milled germ (Zosel, 1981). Note that moisture is generally removed from the germ after the oil has been essentially extracted supercritically.

Flour properties

Flours removed from the extractor had very low moisture (2.0–3.5%) and were very friable. Pin-milling these flours at 9,000 rpm (one pass) produces a mean particle size of less than 75 microns (200 mesh). Particle size is important for dispersibility and homogeneous mixing of the protein flour in beverages, doughs, and batter foods.

Proximate analyses of extracted corn germ flours (all from the same batch) are given in Table 1. The efficiency of the SC-CO_2 extraction is essentially the same for both tempered and "as-is" germs (samples 1 and 2). Only small amounts of triglycerides remained in these SC-CO_2-extracted flours. In comparison, it is evident that SC-CO_2 was more effective than hexane in reducing both the total residual lipid level and the peroxidase activity. Reducing particle size by wet-grinding the germ in hexane (sample

$SC\text{-}CO_2$ EXTRACTION OF DRY MILLED GERM . . . From page 232

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